ELECTROCONDUCTIVE TEXTILES

FIELD OF THE INVENTION

5   The present invention relates to electroconductive textiles and methods for producing electroconductive textiles.

BACKGROUND OF THE INVENTION

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It has been recognized for some time that the electrical properties of inherently conductive polymers (ICPs) can best be exploited by their incorporation into host structures that provide the required mechanical and

15   physical properties for a given application. Textiles produced from both naturally occurring and synthetic fibres are suited to this purpose.

Inherently conductive polymers immobilised by a

20   textile substrate could be used for a number of applications. These electroconductive textiles can be used in the production of clothing articles which function as wearable strain gauges for use in biomechanical monitoring, or direct biofeedback devices for sports

25   training and rehabilitation. In these articles physical changes in the textile cause changes to electrical resistance or electrical conductivity which can then be monitored. Other applications include the production of clothing articles which change their thermal insulation or

30   moisture transport characteristics in response to changing climatic conditions. Electroconductive textiles can also be used in applications where antistatic or EMI shielding properties are required. A further application is for use in heating devices such as car seats, car seat covers and

35   gloves.

Currently known textile materials coated with

inherently conductive polymers suffer from a number of
disadvantages.

    Ideally, electroconductive textiles should contain
5   electronic components seamlessly integrated into the
conventional textile structure, exhibit stable electrical
properties, withstand normal wear, and be launderable.
There are currently no commercially available conducting
polymer coated textiles that fulfil all of these
10 requirements. It would also be desirable for conventional
textile dyeing or printing techniques to be used in the
production of the electroconductive textile, however this
is usually not possible due to the poor solubility
properties of the inherently conductive polymers and some
15 monomer precursors in water.

    One current method used for preparing
electroconductive textiles involves *in situ* polymerisation
of the inherently conducting polymer onto a substantially
20 non-conductive textile substrate. However, there is no
apparent bonding between the non-conductive textile and
the inherently conductive polymer (including some monomer
precursors from which the polymer is formed).
Consequently, the polymers can be easily abraded or
25 displaced from the textile, or during laundering the
textile may suffer from rapid loss of conductivity. In
addition, the polymer component of the electroconductive
textile can easily change oxidation state or be dedoped.
Moreover, the polymer coating containing the conductive
30 material can significantly change the properties of the
non-conductive textile to which it is applied.

    For similar reasons, the use of curing agents to
affix conductive polymers onto the surface of textile
35 substrates is also disadvantageous.

    Another technique currently used for the production

of an electroconductive textile involves making the
textile fibres from the conductive polymer itself and
forming a fabric from the fibres. However, the nature of
conductive polymers is such that the fibres are relatively
5   brittle and inextensible and textiles formed from these
fibres also suffer from these limitations. In addition,
since the conductive polymer component of an
electroconductive textile is much more expensive than non-
conductive textiles such as cotton, wool and nylon, the
10   electroconductive textile produced by this method is
prohibitively expensive.

Another technique explored more recently has
involved the polymerisation of conducting polymers onto
15   the chemically activated surface of a textile material.
This requires actual pre-phosphonylation of the textile
material (such as polyethylene) to create a chemically
activated textile which will bond with the conductive
polymer. Although this gives rise to a strong bond between
20   the textile and the inherently conductive polymer,
phosphonylation changes the feel or "hand" of the textile.

The existing methods also suffer from the fact that
there are limited means besides altering the level of
25   doping to control the conductivity of the
electroconductive textile.

Another problem associated with the current systems
for producing electroconductive textiles relates to the
30   nature of the inherently conductive polymers themselves.
A large proportion of known inherently conductive polymers
are insoluble in solvents, particularly water. This makes
it very difficult to bring the conductive polymers into
intimate contact with the textile.
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Accordingly, it is an object of the present
invention to provide a new approach for the production of

electroconductive textiles that address these problems.

SUMMARY OF INVENTION

5   According to the present invention there is provided
an electroconductive textile comprising:
          -    a non-conductive textile,
          -    a macromolecular template which is bonded to or
               entrapped in the non-conductive textile, and
10   -   a conductive polymer which is ordered by and
bonded to the macromolecular template;
          such that the macromolecular template binds the
conductive polymer to the non-conductive textile.

15   By using a macromolecular template of a type that is
capable of directly binding to or being directly entrapped
within the non-conductive textile (i.e. not by affixing
with an interposed curing agent), a number of advantages
are achieved. Firstly, the macromolecular template will
20   improve the conductive nature of the conductive polymer by
inducing order in the conductive polymer. In addition,
the macromolecular template and the reaction conditions
for directly coupling the macromolecular template to the
conductive polymer can be chosen to control the level of
25   conductivity of the conductive polymer.

          Another advantage of using a macromolecular template
is that a suitable preformed templated conducting polymer
can be prepared that will make the conductive polymer
30   soluble in the desired solvent, so as to facilitate the
bringing of the conductive polymer into contact with the
non-conductive textile. Similarly, a mixture of the
macromolecular template with the subunits from which the
conducting polymer is made enables solubilization of the
35   subunits in the desired solvent so as to facilitate the
bringing of the conductive polymer into contact with the
non-conductive textile. This allows for conducting

polymers to be applied to textiles using techniques that were otherwise not possible, and without the need for a curing step to bind the conducting polymer to the textile. Various other advantages associated with the use of the

5   macromolecular template will be explained in further detail below.

According to the present invention there is also provided a method for preparing an electroconductive

10   textile from a non-conductive textile and polymer subunits which, when polymerised, form a conductive polymer, the method comprising the steps of:

(i) polymerising the polymer subunits in the presence of a macromolecular template to form the conductive

15   polymer bound to the macromolecular template; and

(ii) contacting the macromolecular template with the non-conductive textile to effect bonding of the macromolecular template to the non-conductive textile.

20   As will be explained in further detail below with reference to the main alternative techniques for preparing the electroconductive textile, step (ii) outlined above can be conducted prior to, or following step (i). Consequently, the applicant envisages three main methods

25   by which the electroconductive textile can be prepared.

The first alternative method for preparing the electroconductive textile comprises the steps of:

(a) contacting the macromolecular template with the

30   non-conductive textile to effect bonding of the macromolecular template to the non-conductive textile, and

(b) contacting the polymer subunits with the macromolecular template bound to the non-conductive textile, and polymerising the polymer subunits to form the

35   conductive polymer bound to the macromolecular template and to the non-conductive textile via the macromolecular template.

The second alternative method for preparing the electroconductive textile comprises the steps of:

(a) contacting the non-conductive textile, the macromolecular template and the polymer subunits with one another to effect bonding of the macromolecular template to the non-conductive textile, and bonding of the macromolecular template to the polymer subunits, and

(b) polymerising the polymer subunits to form the conductive polymer which is bound to the non-conductive textile via the macromolecular template.

The third alternative method for preparing the electroconductive textile comprises the steps of:

(a) contacting the macromolecular template with the polymer subunits and polymerising the polymer subunits to form the conductive polymer bound to the macromolecular template, and

(b) contacting the macromolecular template with the non-conductive textile to effect bonding of the macromolecular template to the non-conductive textile, with the conductive polymer bound to the non-conductive textile via the macromolecular template.

According to the present invention there is also provided a new use of a macromolecular template having properties which makes it capable of binding with a non-conductive textile, in the preparation of an electroconductive textile from the non-conductive textile and polymer subunits which, when polymerised, form a conductive polymer.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention is described further by way of example with reference to the accompanying drawings in which:

Figure 1 illustrates schematically the three main

techniques for forming the electroconductive textile of
the present invention; and

        Figure 2 is a UV/VIS Spectrum of PMAS and templated
PMAS/PAn treated wool/nylon/Lycra®.

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DETAILED DESCRIPTION OF THE INVENTION

        As explained above, there are three main techniques
for forming the electroconductive textile of the present
10   invention.   These are schematically illustrated in Figure
1.

        The first alternative method represented by (I)
involves applying the macromolecular template represented
15   by A to the textile, represented by T.   In a second step
the polymer sub-units represented by B are brought into
contact with the macromolecular template A bound to the
non-conductive textile T, and polymerisation is effected
while in situ in the textile to produce the
20   electroconductive polymer C.   The final product, which may
need to be subjected to further treatment steps such as
doping, is the electroconductive textile X.

        The second alternative method for preparing the
25   electroconductive textile X is represented by (II).
According to this method, the macromolecular template A is
contacted with the polymer subunits B, prior to or at the
same time that it is contacted with the textile T.   This
will yield a treated non-conducting textile T containing
30   the macromolecular template A and polymer subunits B.   In
a second stage, polymerisation of the subunits B is
effected to produce the electroconductive polymer C and
thus yield the electroconductive textile X.

35   The third alternative method for preparing the
electroconductive textile X is represented by (III).

According to this method, the macromolecular template A is brought into contact with the polymer subunits B, which are then polymerised to yield a preformed templated conductive polymer as represented by Y. The preformed templated polymer Y is then applied to the textile to yield the electroconductive textile X.

It is to be understood that the macromolecular template A and the polymer subunits B may constituted by mixtures of different materials.

In the following we have explained the meaning of the various terms used in the specification for complete understanding of the scope of the invention.

Non-conductive Textile Material

The term "textile material" or "textile" is used herein in its broadest sense and includes yarns, threads, fibres, cords, filaments, fabrics, cloths and materials that have been woven, knitted, felted, thermally bonded, hydroentangled, spunbonded, meltblown, electrospun or formed from other nonwoven processes or formed from the foregoing, and combinations thereof.

The term "non-conductive" means that the textile material is non-conductive, or has very low conductivity. Non-conductive is defined as having a surface resistivity of greater than 10^{11} $\Omega/\square$. Conductivity is the converse of resistivity, which is measured in the art in units of ohms per square ($\Omega/\square$).

The textile material may be formed from natural or synthetic fibres or a combination of the two. Natural fibres include, notably, cellulosic fibres and

proteinaceous fibres, such as cotton, hemp and wool.
Synthetic fibres include the range of polymers that have
been made in a fibre form, including polyalkylenes (and
homopolymers or copolymers; examples of the homopolymers
5 being polyacrylonitrile and polypropylene); polyamides
including nylon (such as nylon 6 and nylon 66), Kevlar®
and Nomex®; polyurethanes, including polyurethane block
copolymers (such as Lycra®); polyureas (and block
copolymers thereof such as polyurethaneureas); polyesters
10 such as polyethylene terepthalate (PET); and synthetic
cellulose-derived fibres, such as rayon, and combinations
thereof.

According to one embodiment, the non-conductive
15 textile is a natural fibre-containing textile, suitably a
wool-containing textile.

Due to the choice of templates and conductive
polymers used, the non-conductive textiles do not need to
20 be subjected to a functionalisation reaction (sometimes
required in the art) for fixation purposes. Thus,
according to one embodiment, the non-conductive textiles
used in the present invention are not subjected to a
functionalisation reaction to make it possible for a
25 covalent bond to be formed between the textile and the
macromolecular template on later application of the
macromolecular template. Preferably, the non-conductive
textile also contains no phosphonylation.

30   Similarly, the textiles can be made
electroconductive by techniques that do not require a
curing step to bind the conducting polymer to the textile.
This is also an advantage of the present invention.

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Conductive Polymer

      The term "conductive polymer" is used broadly to
refer to any of the class of conductive polymers known in
the art. These are sometimes referred to as "inherently
5   conductive polymers" or "intrinsically conductive
polymers".

      Conductive polymers are unsaturated polymers
containing delocalised electrons and an electrical charge.
10 Conductive polymers may be positively or negatively
charged (cationic or anionic), and are associated with
counter ions referred to as the dopant. Polymers in the
main class of conductive polymers are polymerised from
their polymer subunits by oxidation. These will be
15 referred to as the oxidatively polymerised conductive
polymers.

      The term "conductive polymer" is used in its
broadest sense to refer to doped and dedoped conductive
20 polymers, and therefore it encompasses any of the polymers
which form polaronic (including bipolaronic) moieties.
Generally, polarons are the charge carrying species which
are generated by the oxidation of the conjugated polymer
backbone.

25

      Examples of suitable conductive polymers are
polypyrrole and its derivatives, polythiophene and its
derivatives, phenyl mercaptan and its derivatives,
polycarbazole and its derivatives, polyindole and its
30 derivatives and polyaniline and its derivatives, or
combinations thereof. Suitable derivatives are those that
contain functional groups, such as a methoxy group.
Examples within the range of other optional functional

groups are alkyl, alkenyl, alkynyl, aryl, halo, haloalkyl,
haloalkenyl, haloalkynyl, haloaryl, hydroxy, alkoxy,
alkenyloxy, aryloxy, benzyloxy, haloalkoxy,
haloalkenyloxy, haloaryloxy, nitro, nitroalkyl,

5 nitroalkenyl, nitroalkynyl, nitroaryl, nitroheterocyclyl,
amino, alkylamino, dialkylamino, alkenylamino,
alkynylamino, arylamino, diarylamino, benzylamino,
dibenzylamino, acyl, alkenylacyl, alkynylacyl, arylacyl,
acylamino, diacylamino, acyloxy, alkylsulfonyloxy,

10 arylsulfenyloxy, heterocyclyl, heterocycloxy,
heterocyclamino, haloheterocyclyl, alkylsulfenyl,
arylsulfenyl, carboalkoxy, carboaryloxy, mercapto,
alkylthio, benzylthio, acylthio, sulfonate, carboxylate,
phosphonate and nitrate groups or combinations thereof.

15 The hydrocarbon groups referred to in the above list are
preferably 10 carbon atoms or less in length, and can be
straight chained, branched or cyclic.

Dopant

20   Dopants or doping agents provide the counter ions
which are associated with the conductive polymers. These
may be derived from strong acids such as p-toluene
sulfonic acid, naphthalene disulfonic acid, methane
sulfonic acid, chloromethyl sulfonic acid, fluoromethyl

25 sulfonic acid, oxalic acid, sulfosalicylic acid and
trifluoroacetic acid. However, as explained below, the
dopant may be provided by the macromolecular template or
another agent (for example, the acid moiety of the
functional groups present in any reagent used in forming

30 the electroconductive textile). Oxidizing agents such as
ammonium persulfate, ammonium peroxydisulfate, iron (III)
chloride, salts of permanganates, peracetates, chromates
and dichromates may contribute to the doping effect.

Polymer Sub-units

The term "polymer sub-unit" is used herein to refer to monomers, dimers, multimers (eg oligomers) and mixtures

5   thereof that, upon polymerisation, form a polymer. In the context, the polymer formed may be a conductive polymer. The polymer subunits which form the conductive polymer may be the same or different. Furthermore, the dimer and multimer may be formed from monomer units which are the

10 same or different. Consequently, the conductive polymer may be a homopolymer or a copolymer.

Examples of suitable polymer sub-units are aniline, thiophene, bithiophene, terthiophene, pyrrole, phenyl

15 mercaptan, indole, carbazole, and derivatives thereof. Pyrrole, thiophene and aniline and their derivatives are particularly preferred.

Polymer

20 The term "polymer" is used in its broadest sense to encompass homopolymers, copolymers, oligomers and so forth, unless the context is to the contrary.

Macromolecular template

25 The term "molecular template" refers to any chemical, compound, substance or mixture thereof that provides a template upon which, or in relation to which, the polymer subunits of the conductive polymer will preferentially align to induce the desired orientation of

30 the subunits for forming the conductive polymer. For instance, where the polymer is to be preferentially para-directed during synthesis, an appropriate template is one which causes the polymer subunits to be aligned to form a

complex with the template that leads to mostly para-directed synthesis, with limited alternative branching. The prefix "macro" means that the molecular template is a macromolecule in size. A macromolecule is defined as a

5   molecule of high relative molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from the molecules of low relative molecular mass. To avoid any doubt, we note that porphyrins, large dyestuffs and

10   similar compounds are encompassed by the expression "macromolecule". Generally, macromolecules have a molecular weight of about 1000 or more, suitably 1200 or more. The term "macromolecular template" encompasses polymeric molecular templates, and indeed particular

15   embodiments of the invention utilise polymeric molecular templates.

Although a large range of substances are known to function as "molecular templates" in a broad sense, it is

20   noted that the macromolecular templates of the present invention must be compounds that are capable of bonding with or being entrapped within the non-conductive textile. Consequently, not all materials described in the prior art as molecular templates function as macromolecular

25   templates as defined in the present application.

The templates of the present invention are "molecular" in that they provide template-guiding on a molecular level, rather than a physical level.

30

The macromolecular templates provide strands or a structured surface area upon which the polymer subunits that form the conductive polymer can be bound in an

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ordered fashion by non-covalent intermolecular interactions to form a stable molecular complex.

The macromolecular templates may be non-conductive
5   or conductive. The use of conductive macromolecular templates is of particular interest, as they can add to the conductive properties of the electroconductive textile themselves.

10   Electrically conductive macromolecular templates, and particularly polymeric molecular templates, encompass conductive polymers containing one or more acid, ester or salt (electrolyte) groups, and derivatives thereof. The acid or ester group is one that contains a carbon, sulfur,
15   nitrogen or phosphorous to oxygen double bond, and a single bond from said carbon, sulfur, nitrogen or phosphorous atom to another oxygen (or sulfur or nitrogen) atom. Accordingly, this class of functional groups includes sulfates, sulfonates, carboxylates, phosphonates,
20   nitrates, amides, and the acid equivalents (such as sulfonic acid, carboxylic acid, and so forth) and derivatives thereof. Sulfonate and sulfate groups are preferred. Such conductive macromolecular templates containing sulfonate and/or sulfate may be fully or
25   partially sulfonated.

These conductive polymers may contain any other functional groups, such as a methoxy group. Examples within the range of other optional functional groups are
30   alkyl, alkenyl, alkynyl, aryl, halo, haloalkyl, haloalkenyl, haloalkynyl, haloaryl, hydroxy, alkoxy, alkenyloxy, aryloxy, benzyloxy, haloalkoxy, haloalkenyloxy, haloaryloxy, nitro, nitroalkyl,

nitroalkenyl, nitroalkynyl, nitroaryl, nitroheterocyclyl,
amino, alkylamino, dialkylamino, alkenylamino,
alkynylamino, arylamino, diarylamino, benzylamino,
dibenzylamino, acyl, alkenylacyl, alkynylacyl, arylacyl,

5   acylamino, diacylamino, acyloxy, alkylsulfonyloxy,
arylsulfenyloxy, heterocyclyl, heterocycloxy,
heterocyclamino, haloheterocyclyl, alkylsulfenyl,
arylsulfenyl, carboalkoxy, carboaryloxy, mercapto,
alkylthio, benzylthio and acylthio. The hydrocarbon

10   groups referred to in the above list are preferably 10
carbon atoms or less in length, and can be straight
chained, branched or cyclic.

A preferred class of conductive macromolecular

15   templates encompasses the sulfonated polyanilines,
sulfonated polypyrroles, and sulfonated polythiophenes,
and derivatives thereof. The expression "derivatives
thereof" means that the compounds contain one or more of
the functional groups outlined above. One particularly

20   useful molecular template within this class is poly 2-
methoxyaniline-5-sulfonic acid (PMAS).

Examples of non-conductive macromolecular templates
which can be used are polyvinylsulfonate, polystyrene

25   sulfonates, biologically active polymers such as heparin,
chondroitin sulfate and dextran sulfate, as well as large
multicharged ions such as calixarenes, cyclodextrins and
selected polymeric textile dyestuffs. Although these
compounds are non-conductive, they can provide dual

30   functions. For instance, these compounds function as
macromolecular templates, and may also function as a
dopant or dye for colouring of the textile.

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Thermally sensitive polyelectrolytes such as poly-2-acrylamido-2-methyl propane sulfonic acid (PAMPS) and co-polymers comprising the AMPS monomer are other examples of macromolecular templates which can be used.

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Redox containing polyelectrolytes such as polyvinyl ferrocene sulfonate are other examples of macromolecular templates that provide a function in addition to the molecular template function. Other classes of
10 macromolecular templates that provide a dual function comprise UV absorbers, fluorescent whitening agents, stain blocking agents and shrinkproofing polymers which are also macromolecular templates. It is to be noted, however, that not all UV absorbers, fluorescent whitening agents,
15 stain blocking agents and shrinkproofing polymers are or can act as macromolecular templates.

As mentioned above, the macromolecular template may be conductive, and in this instance the macromolecular
20 template can be either a cationic or anionic conductor. Cationic macromolecular templates may be used to bind an anionic conductive polymer to the non-conductive textile. Similarly, an anionic macromolecular template may be used to bind a cationic conductive polymer to the non-
25 conductive textile.

Polyelectrolytic molecular templates are the preferred class of macromolecular templates, and an example includes PMAS.

30

In a preferred embodiment, the macromolecular template can provide an environment for facile oxidation of the polymer subunits to form the conductive polymer.

Bound

The term "bound" or "bonded" or "bind" refers to
non-covalent or covalent intermolecular interactions
5   between two compounds. Hydrogen bonding is encompassed by
this term. This term is used in the sense of direct
bonding between two compounds without an interposed agent
such as a curable adhesive. Covalent bonding refers to
the direct interaction between the macromolecular template
10   and the textile, or the macromolecular template and the
conducting polymer. Non-covalent bonding encompasses ionic
intermolecular interactions sufficient to bond one surface
directly to the other without any interposed agent such as
an adhesive.
15

One test for determining whether the conductive
polymer is bound to the non-conductive textile via the
macromolecular template only as required herein involves
subjecting the product to sonication to detect evidence of
20   loss of the conductive polymer from the textile. Removal
of conductive polymer during the sonication test indicates
that the conductive polymer is not bound by the
intermolecular interactions. Another simple test
correlates to the standard test used in fabric dyeing to
25   determine whether a colouring agent has bonded to the
fabric or not. This involves rubbing the textile against
white fabric. Marking of the white fabric demonstrates
that the dye has not bonded to the fabric.

30   In the non-printing methods for applying the
conductive polymer to the non-conductive textile, the
mechanism of binding is preferably not a curing mechanism.

Entrapment

        The expression "entrapped in" refers to the
situation where the macromolecular template forms an
interpenetrating network through the textile fibre matrix.
5   The expression "interpenetrating network" is well
understood in the field of polymers and is used in the
same sense here.   It involves the polymer chains extending
into the textile fibre matrix and being entrapped therein
without direct covalent chemical bonding.

10

Polymerisation

        The polymer sub-units are polymerised by any process
appropriate for the particular monomers involved. This
encompasses addition polymerisation or condensation
15 polymerisation, with free radical initiation, where
required, produced by redox reaction, light or microwave.
Usually the polymerisation is by way of addition
polymerisation for the production of the conductive
polymer.

20

        The contacting of the various components with one
another in the methods of the invention can be achieved by
any appropriate technique. Advantageously this is
achieved by one of the conventional textile dyeing
25 techniques, including padding, exhaustion, printing and
coating including foam applications.

Products made from electroconductive textiles
        The electroconductive textiles of the present
30 invention may be used to manufacture articles requiring
electroconductive properties. The articles may be made
partly or entirely from the electroconductive textile.
Examples include gloves, car seats, heating panels for car

seats, protective clothing, hosiery, and other apparel
items, footwear, headgear, strain gauges, energy storage
devices such as batteries or capacitors, and energy
conversion devices.

5

The present invention provides additional
functionality, and overcomes compatibility issues of some
conductive polymers with non-conductive textiles when the
prior art is employed. The present invention also provides
10   a means of locating the conductive polymer either inside
the non-conductive textile or on its surface, thereby
allowing users to further tailor electroconductive
textiles to suit individual applications and requirements.

15   Other Product and Process Options
As indicated above, the macromolecular template can
itself be a conductive polymer. In this situation, the
electroconductive textile comprises a non-conductive
textile, having a conductive macromolecular template
20   bonded thereto, and a conductive polymer (which may be the
same substance or a different substance to the
macromolecular template) bonded thereto. It is also
possible, according to this embodiment or any other
embodiment, to apply to the 3 component electroconductive
25   textile one or more further layers of conductive polymer.

EXAMPLES

A number of preferred embodiments are described by
30   reference to the following non-limiting examples.

Most of the examples provided below utilise poly 2-
methoxyaniline-5-sulfonic acid (PMAS) as the

macromolecular template. This macromolecular template is
itself a conductive polymer, and therefore some electrical
resistivities are reported for textiles to which the
macromolecular template has been applied. However, to
5   avoid misunderstanding, it is noted that not all
conductive polymers are capable of functioning as a
macromolecular template which both provide the templating
function for the conductive polymer, and bond to a non-
conductive textile. Nevertheless, as these precursors in
10   the preparation of the electroconductive textiles of the
present invention do have conductive properties, their
levels of electrical resistivity have been reported on
occasion in the following examples.

15   Furthermore, in the examples, the % exhaustion (for
example, of molecular template onto non-conductive
textile) was determined from UV/VIS absorption
spectroscopy. For PMAS, this was calculated from the
474nm absorption peak. The measurements were taken at the
20   end of the process step (eg after 4 hours and 30 minutes
application time). This is confirmed in the Tables where *
is marked.

           The values for electrical surface resistivity
25   reported were determined using a modification of the AATCC
Test Method 76 - 1995 Electrical Resistivity of Fabrics,
and represent the mean and standard deviation of 3
readings on a single textile treatment. The electrical
resistance of the treated fabrics was measured on a
30   measurement rig consisting of 2 copper bars spaced 1.5cm
apart embedded in a Perspex base and 2 copper bars which
sat atop the fabric. The textile sample had been
conditioned at 20°C and 65%RH for a period of 2 hours

before measurement. After placement of the textile between
the copper bars, a 1kg weight was placed atop the rig, and
an electrical resistance measurement was taken after 60
seconds. Electrical resistance values were converted to
electrical surface resistivity, and quoted as $\Omega/\square$.

1.   FIRST ALTERNATIVE METHOD FOR FORMING
      ELECTROCONDUCTIVE TEXTILE

1.1   Step 1: Application of Macromolecular Templates to
       Non-Conductive Textiles

       In this Section we demonstrate methods for applying
the macromolecular template of the preferred embodiment of
the invention to a non-conductive textile. Whilst this
corresponds directly to the first step of the first
alternative method for forming the electroconductive
textile of the invention, the same techniques apply to any
of the steps of the second and third alternative methods
(illustrated in Figure 1) in which a macromolecular
template is contacted with the non-conductive textile,
irrespective of whether or not the macromolecular template
has already been contacted with the polymer subunits.

1.1.1 Exhaust Application of PMAS onto Wool-based Textiles

       PMAS [10% on mass of fabric (omf)] was applied to a
scoured chlorine-Hercosett treated wool knit textile using
an Ahiba Texomat Laboratory Dyeing Machine with the wool
textile being wound onto a spindle and submerged in the
application liquor. A liquor:goods ratio of 50:1 was used
and the PMAS application was made to 2g sample of textile
which had been wet out prior to use by soaking at room
temperature for 10 minutes in 1g/L Lissapol TN450 (ICI,

non-ionic surfactant) followed by a distilled water rinse
and a final 10 min soak in acid solution at the desired
pH.

5   The PMAS solution was adjusted to pH 1.4 by the
drop-wise addition of 10% w/v H_2SO_4 to the stirred
solution. The wool textile was introduced to the
application bath at 40°C, heated to 90°C over 30 minutes,
and the temperature maintained for a further 4 hours. The
10   textile sample was then removed from the application
liquor and rinsed in cold tap water until no signs of
"bleed" were evident. Excess water was removed and the
sample was air-dried at room temperature overnight prior
to measurement of the electrical resistivity.
15

        This basic process was used for the application of
the macromolecular template to the non-conductive textile
unless otherwise stated.

20   1.1.2 Variation of Application pH

        The process outlined in 1.1.1 above was repeated
with modification of the initial pH of the PMAS
application liquor. The results of these trials are
25   demonstrated in Table 1.

Table 1:

Initial pH	Final pH	Final % PMAS Exhaustion*	Textile Electrical Resistivity
2.7	4.2	50.0	454 +/- 59 GΩ/□
2.0	2.5	52.7	8.3 +/- 0.3 GΩ/□
1.8	2.0	60.3	1.3 +/- 0.1 GΩ/□
1.6	1.8	71.5	334 +/- 29 MΩ/□
1.4	1.5	86.3	160 +/- 11 MΩ/□

These trials demonstrate that PMAS uptake is
dependent upon the application pH. Lowering the initial pH
results in increased uptake of the PMAS and decreased
electrical resistivity of the treated textile.

5

Non-conductive textiles other than wool can be
subjected to an application pH of less than pH 1.4 due to
better stability of the textile in acid at the process
temperatures. Wool non-conductive textiles, however, are
10 preferable treated at pH 1.4 or above. Under these
conditions the wool textiles produced were structurally
intact, with no obvious weakening of the textile
integrity. The coated textiles could be stretched up to
70%, without tearing.

15

1.1.3 Variation in Application Temperature

The process outlined in 1.1.1 above was repeated
with modification of the temperature of the PMAS
20 application liquor. The results of these trials are set
out in Table 2.

Table 2:

Appl. Temp. (°C)	Initial pH	Final pH	Final % PMAS Exhaustion*	Textile Electrical Resistivity
60	1.4	1.4	38.0	14.4 +/- 0.5 GΩ/□
70	1.4	1.4	38.7	2.4 +/- 0.1 GΩ/□
80	1.4	1.4	51.9	410 +/- 21 MΩ/□
90	1.4	1.5	86.3	160 +/- 11 MΩ/□
100	1.4	1.5	100.0	828 +/- 32 MΩ/□

25   Higher application temperatures are preferred for
maximising uptake of the macromolecular template, although
ultimately the temperature used may be influenced by other

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factors such as electrical resistivity and textile
deterioration.

1.1.4 Variation in Acid Used to Adjust pH

The standard method outlined in 1.1.1 for the uptake
of PMAS on wool was repeated with the substitution of the
sulfuric acid with other acids. The result of this trial
is set out in Table 3.

Table 3:

Acid	Initial pH	Final pH	Final % PMAS Exhaustion*	Textile Electrical Resistivity
H_2SO_4	1.4	1.4	96.8	227 +/- 13 MΩ/□
HCl	1.4	1.5	99.9	4.0 +/- 3.2 GΩ/□
p-Toluene Sulfonic Acid	1.4	1.5	92.3	280 +/- 1 MΩ/□
10-Camphor Sulfonic Acid	1.4	1.5	87.3	176 +/- 1 MΩ/□

1.1.5 Variation in PMAS Concentration

The process outlined in 1.1.1 above was repeated
with modification to the PMAS concentration, measured as a
percentage based on the mass of the non-conductive
textile. The results of these trials are set out in Table
4.

Table 4:

Initial PMAS Conc. (% omf)&	Final pH	Final % PMAS Exhaustion*	Textile Electrical Resistivity (MΩ/□)
5	1.5	99.4	804 +/- 21
10	1.5	71.1	88.6 +/- 1.9
15	1.4	59.3	71.3 +/- 1.1
20	1.4	46.9	80.9 +/- 1.1

& "omf" refers to "on mass of fabric".

1.1.6 Variation of Macromolecular Template

1.1.6.1   Other Conductive Macromolecular Templates

5

Other water-soluble conductive templates can be used
in place of PMAS. Partially sulfonated polyaniline, with
sulfonation on ~ 80% on the aniline rings was produced
from polyaniline by the method using chlorosulfonic acid.
10 Application of the partially sulfonated polyaniline to
scoured chlorine-Hercosett treated wool knit textile was
performed using the same conditions described in 1.1.1 for
PMAS. This application resulted in an exhaustion of 80.0%
of the partially sulfonated polyaniline onto the textile
15 material, affording it an electrical resistivity of 790
+/-13 MΩ/$\square$.

Similarly, PMAS was substituted by water-soluble
copolymers of the 2-methoxyaniline-5-sulfonic acid monomer
20 (MAS), and aniline (AN). Copolymers with MAS/AN molar feed
mix ratios varying from 19:1 to 4:1 have been prepared and
evaluated. They have been found to provide a similar
conductive effect to PMAS, with electrical resistivities
as low as 35 +/-3 MΩ/$\square$ being recorded for wool knit
25 textile samples prepared from the copolymers by the same
conditions for PMAS.

1.1.6.2   Non-conductive Macromolecular Templates

30 The method outlined in 1.1.1 above was repeated with
the replacement of the PMAS with a range of other
macromolecular templates applied at 10% offer based on
mass of fabric. The results of the exhaustion levels from

- 26 -

this study, as determined by UV/VIS, are set out in Table 5 below:

Table 5:

Macromolecular Template	% Exhaustion level
Basyntan D liquid (BASF)	80
Seicitan D Liquid (Seici)	76
Intan EMS (Alpa)	96
Trupotan R83 (Trumpler)	42
Synthaprett BAP (Bayer)	34
Orotan SN Powder (Bayer)	90
Poly (styrene sulfonic acid/maleic acid) (Polysciences Inc.) 3:1 or 1:1	75-80
Dextran Sulfate	97*

5   * Exhaustion of dextran sulfate was determined by toluidine blue assay. Similar levels of exhaustion of dextran sulfate were obtained for 20, 30, 40 and 50% offers based on mass of wool fabric

1.1.7 Variation of Non-Conductive Textile.

10

The process outlined under 1.1.1 above was repeated with the substitution of the wool textile described there with the following textile composites:

15   wool/nylon/Lycra®;
            wool/polyester;
            nylon;
            nylon/Lycra®; and
            cotton.

20

3 different wool/nylon/Lycra® fabrics were used. They ranged in wool content from 90-97%, nylon 2-8%, and

- 27 -

Lycra® 0.5-1%, and were of approximately 270g/m² density.
These fabrics were manufactured by the applicant, and have
commercially available equivalents.

5   The nylon and nylon/Lycra® were commercially
available textiles obtained from a retailer of fabrics.
The cotton was a scoured fabric that again was knitted by
the applicant, having similar properties to commercially
available cotton fabric.

10

        The wool-based templated textiles produced had
similar electrical resistivity to the 100% wool textiles
reported in 1.1.1 above.

15   1.1.8 Other Application Techniques for PMAS

        Examples 1.1.1 – 1.1.7 all relate to the application
of the macromolecular template to the non-conductive
textile by the exhaust technique, in which the non-
20   conductive textile is saturated in an application liquid
containing the macromolecular template. In the following
we have exemplified other application techniques.

     1.1.8.1   Padding

25

        An aqueous pad liquor (100ml) was prepared
containing 33.3g/L PMAS at 20°C. The unadjusted pH of the
pad liquor prior to use was 1.2. A 2g sample of wool
textile was wet out prior to being padded by soaking in an
30   aqueous solution of 1g/L Lissapol TN450 (non-ionic
surfactant, ICI) at 20°C for 10 minutes. The fabric was
rinsed at room temperature with distilled water and then
passed through squeeze rollers set to provide 100% pickup.

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The damp fabric was then added to the pad liquor, the fabric allowed to become saturated with the liquor over 2 minutes with mild agitation by hand, then withdrawn and passed through squeeze rollers that provided a pickup of

5   225%. These conditions had the effect of applying 7.5% omf PMAS to the textile sample. After this treatment, the sample was placed in an airtight plastic bag and "batched" at 20°C in the dark for 24 hours. Following this period, the sample was removed from the plastic bag and rinsed in

10   cold tap water until free of "bleed", dried overnight at room temperature and the electrical resistivity of the textiles was then measured to be 870 +/- 11 MΩ/□.

1.2   Step 2: Contacting of Templated Textile with Polymer
15   Subunits and *In situ* Polymerisation

1.2.1 *In Situ* Polymerisation of Aniline on PMAS Pre-
       treated Wool Textiles

20   A sample of the PMAS treated textile of Example 1.1.1 was wound onto a spindle and wet out by soaking at room temperature for 10 min in 1 g/L Lissapol TN450 (ICI, non-ionic surfactant) followed by a distilled water rinse. Aniline was added to distilled water (80 ml) and after

25   stirring for 30 min, the pH was adjusted to pH 1.4 by the drop-wise addition of a 10% w/v solution of sulfuric acid and the final volume was made up to 85 ml.

            The spindle was placed in the aniline solution and
30   stirred for 15 min using an overhead stirrer (60 rpm). The *in situ* polymerisation was brought about by the drop-wise addition of a solution of ammonium persulfate in distilled water (15 ml) over a 15 min period to the

mixture, which was then left to stir for a further 16 h at
room temperature. After the 16 h, the sample was
removed, rinsed in cold water and allowed to air dry at
room temperature. A significant decrease in electrical

5   resistivity from 160 MΩ/□ for the PMAS treated wool to 69
KΩ/□ for the templated textile after the *in situ*
polymerisation process was observed.

1.2.2 Variation in PMAS:Aniline Ratio

10

The method outlined in 1.2.1 above was repeated with
modifications to the molar PMAS:aniline ratio. The results
are set out in Table 6. The results show that there is an
optimum molar ratio of PMAS:aniline of approximately 1:2,

15   at a constant aniline:oxidant ratio of 1:0.25.

Table 6:

PMAS:Aniline Ratio	PMAS:Aniline:Oxidant Ratio^	Templated Textile Electrical Resistivity(MΩ/□)
1:1	1:1:0.25	8.0
1:2	1:2:0.5	1.9
1:3	1:3:0.75	3.4

^   Polymerisation using constant 1:0.25 aniline: ammonium
persulfate ratio in each case.

20

1.2.3 Variation of Aniline:Oxidant Ratio

The method outlined in 1.2.1 above was repeated with
modifications to the aniline:oxidant molar ratio, where

25   the PMAS:aniline ratio was held constant at 1:2. The
results are set out in Table 7. It was found that the
range of ratios between 1:0.25 - 1:0.5 afforded the lowest
electrical resistivity for wool-based textiles.

Table 7:

Aniline:Oxidant Ratio	PMAS:Aniline:Oxidant Ratio	Templated Textile Electrical Resistivity
1:0.125	1:2:0.25	3.7 +/- 0.3 MΩ/□
1:0.25	1:2:0.5	136.2 +/- 0.8 KΩ/□
1:0.5	1:2:1	154.6 +/- 16 KΩ/□
1:1	1:2:2	2.9 +/- 0.5 MΩ/□

1.2.4 Variation in PMAS Concentration

5   The method outlined in 1.2.1 above was repeated,
with the modification that the PMAS treated textiles used
were not those of Example 1.1.1, but those of 1.1.5,
having a concentration of PMAS (measured as a percentage
based on the mass of the non-conductive textile $_T$ that is
10 %omf) of 5%, 10%, 15% and 20%. The results are set out in
Table 8. Increasing the PMAS concentration from 5-15% omf
results in a decrease in the electrical resistivity of
templated textiles. However, further increases in PMAS
concentration were shown to have only marginal influence.

15

Table 8:

Initial PMAS Conc. (% omf)	Final % PMAS Exhaustion*	PMAS conc. in Textile (% omf)	Templated Textile Electrical Resistivity (KΩ/□)
5%	99.4	5%	874 +/- 21
10%	71.1	7.1%	126.3 +/- 2.1
15%	59.3	8.9%	87 +/- 1.1
20%	46.9	9.4%	83 +/- 1.1

1.2.5 Variation of Polymerisation Temperature

20   The method outlined in 1.2.1 above was repeated with
modifications to the polymerisation temperature. The
results are set out in Table 9. The molecular templated
textiles were found to have a lower electrical resistivity
when the polymerisation was carried out at ambient
25 temperature.

Table 9:

Polymerisation Temperature (°C)	Templated Textile Electrical Resistivity
38	1.1 +/- 0.1 MΩ/□
23	126.3 +/- 2.1 KΩ/□
2.3	275.0 +/- 18.7 KΩ/□

1.2.6 Variation of polymerisation pH

The method outlined in 1.2.1 above was repeated with modifications to the polymerisation pH. The results are set out in Table 10.

Table 10:

Initial pH	Final pH	PMAS Treated Textile Resistivity (MΩ/□)	Templated Textile Electrical Resistivity
4.0	2.7	79.3	2.2 +/- 0.1 MΩ/□
2.4	2.4	90.2	422 +/- 16 KΩ/□
1.4	1.6	76.6	262 +/- 21 KΩ/□

1.2.7 Variation of Acid Used to Adjust pH of
       Polymerisation Solution

The method of Example 1.2.1 was repeated with the replacement of the sulfuric acid with hydrochloric acid. The results are set out in Table 11.

Table 11:

Acid	Templated Textile Electrical Resistivity (KΩ/□)
H_2SO_4	126.3 +/- 2.1
HCl	558 +/- 5

2   SECOND ALTERNATIVE METHOD FOR FORMING
       ELECTROCONDUCTIVE TEXTILE

2.1   Contacting of PMAS and Aniline to Wool Textile, and
  5   *in situ* Polymerisation of PMAS/Aniline Pretreated
           Textiles.

       A PMAS/aniline mixture was simultaneously applied to
       scoured chlorine-Hercosett treated wool knit textile using
 10   an Ahiba Texomat Laboratory Dyeing Machine. The wool
       textile was wound onto a spindle and submerged in the
       application liquor. The spindle was given constant, steady
       agitation by the dyeing machine during the course of the
       application. A standard liquor:goods ratio of 50:1 was
 15   used throughout, and the application was made to a 2g
       sample of wool which had been wet out prior to use by
       soaking at room temperature for 10 minutes in 1g/L
       Lissapol TN450 (ICI, non-ionic surfactant) followed by a
       distilled water rinse and a final 10 min soak in acid
 20   solution at the desired pH.

       The PMAS/aniline mixture solution was adjusted to pH
       1.4 by the drop-wise addition of acid (10% w/v H_2SO_4) to
       the stirred solution. The wool textile was introduced to
 25   the application bath at 40°C, heated to 90°C over 30
       minutes, and maintained at this temperature for a further
       4 hours. After the completion of the application, the
       mixture was allowed to cool to room temperature. The *in
       situ* polymerisation was brought about by the drop-wise
 30   addition of a solution of ammonium persulfate in distilled
       water (15 ml) over a 15 min period to the mixture, which
       was then left to stir for a further 16 h at room
       temperature. After the completion of the application, the

textile sample was removed from the application liquor and
rinsed in cold tap water until no signs of "bleed" were
evident. Excess water was removed and the sample was air-
dried at room temperature. The wool textiles prepared
using this method had electrical resistivities in the
range from 80 KΩ/□ to 668 KΩ/□.

3   THIRD ALTERNATIVE METHOD FOR FORMING
       ELECTROCONDUCTIVE TEXTILE

3.1   Step 1: Synthesis of Preformed Templated Polymers

       A series of templated polymers were prepared in the
presence of 0.02M PMAS using different concentrations of
aniline, as set out in Table 5. Aniline was added to an
aqueous solution of PMAS and the resulting solution's pH
of about 5.4 was adjusted to pH 2.0 by the addition of HCl
(conc.). The required amount of ammonium persulfate
solution to facilitate the polymerisation (set out in
Table 12) was added drop-wise at such a rate as to
maintain the reaction temperature below 24°C. The thick
polymer solution obtained was stirred overnight and then
dialysed by using 12kD dialysis tubing. After dialysis
the polymer solution was stirred and heated to about 50°C
to concentrate the polymer, and then left to dry by
evaporation in a fume hood. The conductivities of pressed
pellets of the templated polymers were then measured, and
the results are set out in Table 12. Conductivities of
pressed pellets as high as 6.8 S/cm were obtained.

Table 12:

Molecular Templating Concentrations	Oxidant Concentration $(NH_4)_2S_2O_8$	Solid Pellet Conductivity (S/cm)	pH
PMAS + Aniline (0.02M + 0.02M)	0.02M	0.05	2.0
PMAS + Aniline (0.02M + 0.06M)	0.06M	6.8	2.0
PMAS + Aniline (0.02M + 0.08M)	0.08M	5.1	1.9
PMAS + Aniline (0.02M + 0.05M)	0.055M	1.2	2.0
PMAS + Aniline (0.02M + 0.037M)	0.02M	1.0	2.1

3.2   Step 2: Application of Preformed Molecular Template
       to Non-conductive Textile

5

The PMAS/PAn (polyaniline) preformed template and
conductive polymer of Example 3.1 containing
PMAS:Aniline:oxidant ratio 0.02M:0.06M:0.06M was applied
to scoured chlorine-Hercosett treated wool knit textile
using an Ahiba Texomat Laboratory Dyeing Machine. The wool
textile was wound onto a spindle and submerged in the
application liquor, and the spindle was given constant,
steady agitation by the dyeing machine during the course
of the application.   A standard liquor:goods ratio of
50:1 was used throughout this example, and the application
was made to a 2g sample of textile which had been wet out
prior to use by soaking at room temperature for 10 minutes
in 1g/L Lissapol TN450 (ICI, non-ionic surfactant)
followed by a distilled water rinse and a final 10 min
soak in acid solution at the desired pH.

The PMAS/PAn template solution was adjusted to pH
1.4 by the drop-wise addition of acid (10% w/v H_2SO_4) to
the stirred solution. The wool textile was introduced to
the application bath at 40°C, heated to 90°C over 30

minutes, and this temperature maintained for a further 4
hours. After the completion of the application, the
textile sample was removed from the application liquor and
rinsed in cold tap water until no signs of "bleed" were

5   evident. Excess water was removed and the sample was air-
dried at room temperature. The products were found to
have electrical resistivity values in the range of 2.7-
26.7 MΩ/□.

10   3.2 Application of Other Preformed Templates

      The preformed template,
poly(styrenesulfonate)/poly(2,3-dihydrothieno[3,4-b]-1,4-
dioxin (PSS/PEDOT) was applied to the scoured chlorine-

15   Hercosett treated wool knit textile. The wool textile was
wound onto a spindle and submerged in the application
liquor, and the spindle was given constant, steady
agitation during the course of the application.   A
liquor:goods ratio of 60:1 was used and the application

20   was made to a 1g sample of textile which had been wet
prior to use by soaking at room temperature for 10 minutes
in 1g/L Lissapol TN450 (ICI, non-ionic surfactant)
followed by a distilled water rinse and a final 10 min
soak in acid solution at the desired pH.

25

      The PSS/PEDOT template solution was adjusted to pH
1.4 by the drop-wise addition of acid (10% w/v HCl) to the
stirred solution. The wool textile was introduced to the
application bath at 40°C, heated to 90°C over 30 minutes,

30   and this temperature maintained for a further 4 hours.
After the completion of the application, the textile
sample was removed from the application liquor and rinsed
in cold tap water until no signs of 'bleed" were evident.

Excess water was removed and the sample was air-dried at
room temperature. The product was found to have an
electrical resistivity value of 74.8 +/- 3.2 KΩ/□.

5   4   USE OF OTHER MACROMOLECULAR TEMPLATES AND CONDUCTIVE
            POLYMERS.

      Experiments using Method I (see Figure 1) where
polystyrene sulfonate (PSS⁻) (MWt 70,000) is the
10   macromolecular template showed that this polyelectrolyte
can also assist in the incorporation of polyaniline into
wool/nylon/Lycra®. Further experiments also with Method I
showed that by using PMAS as a template, other conducting
polymers could also be incorporated into
15   wool/nylon/Lycra®.

      4.1   *In situ* Polymerization of Other Conducting Polymers
             onto PMAS Treated Wool Fabrics

20   4.1.1 Templating of Polypyrrole onto PMAS-treated Wool
            Fabric

      The PMAS/polypyrrole templated fabric was formed by
in situ polymerisation of pyrrole using method I to PMAS-
25   treated chlorine-Hercosett wool prepared by the procedure
of 1.1.1. (Table 13)

      A sample of the PMAS treated textile of Example
1.1.1 was wound onto a spindle and wet out by soaking at
30   room temperature for 10 min in distilled water. Pyrrole
was added to distilled water (80 ml) and after stirring
for 30 min, the pH was adjusted to pH 1.4 by the drop-wise

addition of a 10% w/v solution of sulfuric acid, and the
final volume was made up to 85 ml.

5   The spindle was placed in the pyrrole solution and
stirred for 15 min using an overhead stirrer (60 rpm).
The *in situ* polymerisation was brought about by the drop-
wise addition of a solution of iron(III) chloride
hexahydrate in distilled water (15 ml) over a 5 min period
to the mixture, which was then left to stir for a further
10   3 h at room temperature. After 3 h, the sample was
removed, rinsed in cold water and allowed to air dry at
room temperature. A significant decrease in electrical
resistivity from 160 MΩ/□ for the PMAS treated wool to 69
KΩ/□ for the templated textile after the *in situ*
15   polymerisation process was observed.

The use of other reagents such as hydrochloric acid,
anthraquinone-2-sulfonic acid, 1,5-naphthalene disulfonic
acid can be used as a replacement for, or in addition to
20   the sulfuric acid to prepare the PMAS/polypyrrole
templated fabrics. Alternatively the polypyrrole can be
formed using ammonium persulfate as oxidant.

Table 13:

PMAS:Pyrrole:oxidant	Templated Textile Electrical Resistance (KΩ/□))
1:2:2	46.2 +/- 0.3
1:4:4	5.0 +/- 0.1

25

4.1.2 Templating of Polythiophenes onto PMAS Treated Wool
       Fabric

The PMAS/poly(3-methylthiophene) template was formed
30   by *in situ* polymerisation of 3-methylthiophene to PMAS

treated chlorine-Hercosett wool (171 +/- 4.3 MΩ/$\Box$)
prepared by the procedure of 1.1.1. The 3-methylthiophene
was added to the PMAS treated wool stirred in chloroform
under nitrogen. To this mixture was added a solution of

5   iron (III) chloride dispersed in chloroform and the
resulting mixture was stirred at 40°C for 2 h. After the
completion of the application, the textile sample was
removed from the application liquor and rinsed in cold tap
water until no sign of "bleed" was evident. Excess water

10   was removed and the sample was air-dried at room
temperature. The product was found to have an electrical
resistivity value of 67 +/- 2.7 KΩ/$\Box$). The reaction can
be carried out using acetonitrile as solvent but an
increased level of electrical resistivity was observed

15   (7.7 +/- 0.3 MΩ/$\Box$).

4.1.3 *In Situ* Polymerisation of Aniline on Dextran Sulfate
       Pre-treated Wool Textiles

20   A sample of the dextran sulfate (20% omf) treated
textile (Table 5) was wound onto a spindle and wet out by
soaking at room temperature with Lissapol TN450 (1
g/L,ICI, non-ionic surfactant) followed by a distilled
water rinse. Aniline (0.01 M) was added to distilled water

25   and after stirring for 1 h, the pH was adjusted to pH 1.4
with hydrochloric acid.

          The spindle was placed in the aniline solution and
stirred for 15 min using an overhead stirrer (300 rpm)at

30   2-3°C. The *in situ* polymerisation was brought about by the
drop-wise addition of a solution of ammonium
persulfate(0.0018M) in distilled water (1 drop/sec) and

the reaction left to stir overnight at 2-3°C.   After the
17 h, the sample was removed, rinsed in cold water and
allowed to air dry at room temperature. The electrical
resistivity for the templated textile after the *in situ*
5   polymerisation process was 134-267 MΩ/□.

4.1.4 *In situ* Polymerisation of Aniline on other Non-
         Conductive Macromolecular Treated Wool Textiles.

10   Several other non-conductive macromolecular template
     materials were also templated with aniline by the same
     method and conditions as described above for dextran
     sulfate. The results of these experiments are shown in
     Table 14.

15

Table 14:

Macromolecular Template	Templated Textile Electrical Resistivity (MΩ/□))
α-Cyclodextrin hydrate sulfated sodium salt	12.5
β-Cyclodextrin hydrate sulfated sodium salt	13.8
4-Sulfonic Calix[6] arene hydrate	4.9

4.2   Templating using the Macromolecular Template as the
        Oxidising Agent

20

4.2.1   Oxidation of Aniline due to the Presence of PMAS
          Treated Wool.

The polymerisation of aniline was carried out in the
25   presence of a PMAS treated textile prepared by the method
     in 1.1.1.   Irradiations of the treated textile in a
     solution of aniline at wavelengths of either 300 or 419 nm
     were conducted.   The washed and dried samples were found

to have a decrease in electrical resistivity of 50%
compared to the original PMAS treated textile.

4.2.2 Oxidation of Pyrrole due to the Presence of PMAS

5   Treated Wool.

To an aqueous solution of pyrrole (140mg in 200ml),
adjusted to pH 1.4 with a 10% solution of HCl, was added a
PMAS treated wool fabric (1.5g, 53 MΩ/$\square$) and the mixture

10   was allowed to stir at room temperature for 48 h in
natural light. The sample was removed, rinsed in cold
water and allowed to air dry at room temperature. The
electrical resistivity for the partially templated textile
was 29 MΩ/$\square$.

15

5   PHYSICAL CHARACTERISATION OF MOLECULAR TEMPLATED
         TEXTILES

5.1   UV-VIS Spectral Evidence of Formation of Molecular

20   Template

The UV-VIS spectra using 1,2-dichlorobenzene of wool
textiles relating to the various stages of the *in situ*
templating process are shown in Figure 2. The increased

25   adsorption of higher wavelengths of the templated systems
is indicative of the formation of the PMAS/PAn molecular
template. The figure also demonstrates that the
characteristic PMAS band at 474 nm has decreased and
absorption around 800 nm typical of polyaniline in the

30   expanded coil form has increased.

5.2   Scotch Tape Test

        Each of the electroconductive textile products
produced in the Examples outlined above was subjected to
5   the standard scotch tape test to assess bonding of the
conductive polymer to the non-conductive textile.
Briefly, the test involves adhering commercially available
scotch sticking tape to the treated textile, peeling the
tape from the treated textile and visually determining
10   whether any polymer has been removed with the tape. All
systems evaluated passed the test with no sign of removal
of the ICP (see Table 15).

Table 15:

Fabric	Scotch tape test
PMAS Wool/nylon/Lycra®	No removal of polymer
PMAS/PPy Wool/nylon/Lycra®	No removal of polymer
PMAS/PAn Wool/nylon/Lycra®	No removal of polymer
PPy Wool/nylon/Lycra®	No removal of polymer
Preformed PMAS/PAn Wool/nylon/Lycra®	No removal of polymer

15

5.3   Effect of Washing on Conducting Polymer Treated
        Textiles

        The PMAS/PAn electroconductive textile prepared by
20   Method I (as represented in Figure 1) was subjected to a
standard wash procedure. The test used was a Modified
Woolmark Test Method 31, Washing of wool textile products:
Standard 7A wash cycle, and was performed in a Wascator
FOM 71 MP washing machine. The sample size was 100x100
25   mm. The results of the washing treatment were compared to
a polyaniline and polypyrrole treated textile of the prior
art which did not contain the macromolecular template.
The results are set out in Table 16.

Table 16 also details the results of an acid treatment conducted on the same textiles. After treatment of the washed samples with aqueous sulfuric acid (pH 1.4),

5   the PMAS/PAn treated textile shows a significant decrease in electrical resistivity whereas the polypyrrole system has increase in electrical resistivity. The polyaniline sample shows no evidence of a decrease in its electrical resistance after the acid treatment.

10

Table 16:

	Polyaniline (PAn)	PMAS	PMAS/PAn	Polypyrrole (PPY)
Starting textile	5.6 MΩ/□	206 MΩ/□	347 KΩ/□	11.2 KΩ/□
Washed textile*	>3.2 GΩ/□	382 MΩ/□	1.35 MΩ/□	27.5 KΩ/□
Acid wash	>3.2 GΩ/□	414 MΩ/□	811 KΩ/□	331 KΩ/□

*   Modified Woolmark Test Method 31, Washing of wool textile products: Standard 7A wash cycle. Sample size was 100x100 mm

15 5.4   Effect of Rubbing on Conducting Polymer Treated Textiles

The colourfastness to dry rubbing of PMAS/PAn electroconductive textile prepared by Method I (as

20 represented in Figure 1) was determined in accordance with Australian Standard 2001.4.3 - Determination of Colourfastness to Rubbing, using an Atlas Crockmeter. This test involves the dry rubbing of treated textiles using a standard undyed cotton textile (1M ISO Cotton

25 Rubbing Fabric, supplied by Australian Wool Testing Authority). In addition to the standard 10 rubs required for the test method, extra rubs were performed. This test

showed that the PMAS/PAn molecular templated textile had
less removal of conducting polymer from the textile due to
abrasion than the polyaniline and polypyrrole treated
textiles. The alternative molecular templated textile,

5   PMAS/PPY had improved rubfastness compared to the textile
treated with only polypyrrole.

Table 17:

	Polyaniline (PAn)	PMAS	PMAS/PAn	PMAS/PPY	Polypyrrole (PPY)
Perpendicular					
10 rubs	4	4	4	4	3-4
20 rubs	3-4	3-4	3-4	3-4	3
30 rubs	3	3-4	3-4	3-4	2-3
40 rubs	3	3-4	3	3-4	2-3
Parallel					
10 rubs	3-4	4-5	4	4	3-4
20 rubs	3	4	3-4	4	3
30 rubs	3	3-4	3-4	3	3
40 rubs	3	3-4	3-4	3-4	3

10   Grey scale ratings 5 to 1 white through to grey. A rating of 5
indicates that no polymer is abraded onto the white cotton test
fabric.

6   *IN SITU* TEMPLATED COATINGS AS WEARABLE TEXTILE
15   STRAIN GAUGES.

The effect on electrical resistance due to the
straining of a range of PMAS/PAn molecular templated
wool/composite textiles was determined. The dynamic

20   calibrations at frequencies up to 3 Hz and over a range of
10-70% strain showed that the results compared well with
those obtained using *in situ* coated polypyrrole on

- 44 -

Nylon/Lycra®. Unlike the polypyrrole-coated materials,
minimal change in electrical resistance responses was
observed over a three-week period for the PMAS/PAn
electroconductive textiles.

5

It will be understood to persons skilled in the art
of the invention that many modifications may be made
without departing from the spirit and scope of the
invention.

CLAIMS:

1.   An electroconductive textile comprising:
        -   a non-conductive textile,
        -   a macromolecular template which is bonded to or
entrapped in the non-conductive textile, and
        -   a conductive polymer which is ordered by and
bonded to the macromolecular template;
such that the macromolecular template binds the conductive
polymer to the non-conductive textile.

2.   The electroconductive textile of claim 1, wherein
the conductive polymer is an oxidatively polymerised
conductive polymer.

3.   The electroconductive textile of claim 1 or claim 2,
wherein the conductive polymer is selected from
polypyrrole and its derivatives, polythiophene and its
derivatives, phenyl mercaptan and its derivatives, and
polyaniline and its derivatives, polyindole and its
deriviates, polycarbazole and its derivatives, or
copolymers or combinations thereof.

4.   The electroconductive textile of any one of claims 1
to 3, wherein the conductive polymer is associated with
one or more dopants or doping agents.

5.   The electroconductive textile of any one of claims 1
to 4, wherein the dopant or doping agent is derived from a
strong acid, the macromolecular template or an oxidizing
agent.

6.   The electroconductive textile of any one of claims 1
to 5, wherein the macromolecular template is a conductive
macromolecular template.

7.   The electroconductive textile claim 6, wherein the conductive macromolecular template is a conductive polymeric molecular template.

5   8.   The electroconductive textile of claim 7, wherein the conductive polymeric molecular template contains one or more acid, ester or salt (electrolyte) groups, or derivatives thereof.

10   9.   The electroconductive textile of claim 7, wherein the conductive polymeric molecular template contains sulfate, sulfonate, carboxylate, phosphonate, nitrate, or amide groups or acid equivalents thereof.

15   10.   The electroconductive textile of claim 7, wherein the conductive polymeric molecular template is sulfonated or sulfated.

     11.   The electroconductive textile of any one of claims 7
20   to 10, wherein the conductive macromolecular template is selected from sulfonated polyanilines, sulfonated polypyrroles, and sulfonated polythiophenes, and derivatives thereof.

25   12.   The electroconductive textile of claim 11, wherein the conductive polymer molecular template contains one or more functional groups selected from the group consisting of alkyl, alkenyl, alkynyl, aryl, halo, haloalkyl, haloalkenyl, haloalkynyl, haloaryl, hydroxy, alkoxy,
30   alkenyloxy, aryloxy, benzyloxy, haloalkoxy, haloalkenyloxy, haloaryloxy, nitro, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroaryl, nitroheterocyclyl, amino, alkylamino, dialkylamino, alkenylamino, alkynylamino, arylamino, diarylamino, benzylamino,
35   dibenzylamino, acyl, alkenylacyl, alkynylacyl, arylacyl, acylamino, diacylamino, acyloxy, alkylsulfphonyloxy,

arylsulfphenyloxy, heterocyclyl, heterocycloxy, heterocyclamino, haloheterocyclyl, alkylsulfphenyl, arylsulfphenyl, carboalkoxy, carboaryloxy, mercapto, alkylthio, benzylthio and acylthio.

13.   The electroconductive textile of claim 7, wherein the macromolecular template is poly 2-methoxyaniline-5-sulfonic acid (PMAS).

14.   The electroconductive textile of claim 7, wherein the macromolecular template is a cationic macromolecular template and the conductive polymer is an anionic conductive polymer.

15.   The electroconductive textile of claim 7 wherein the macromolecular template is an anionic macromolecular template and the conductive polymer is a cationic conductive polymer.

16.   The electroconductive textile of any one of claims 1 to 15, wherein the macromolecular template is a polyelectrolytic molecular template.

17.   The electroconductive textile of any one of claims 1 to 16, wherein the macromolecular template provides an environment for facile oxidation of polymer subunits that form the conductive polymer.

18.   The electroconductive textile of any one of claims 1 to 5, wherein the macromolecular template is non-conductive.

19.   The electroconductive textile of claim 18, wherein the macromolecular template is selected from the group of substances consisting of: polyvinylsulfonate, polystyrene

sulfonate, biologically active polymers, chondroitin
sulfate and dextran sulfate, multicharged ions such as
calixarenes, cyclodextrins, polymeric textile dyestuffs
thermally sensitive polyelectrolytes, redox containing
5   polyelectrolytes, UV absorbers, fluorescent whitening
agents, natural and synthetic tanning agents, lignin and
its derivatives, stain blocking agents and shrinkproofing
polymers, with the proviso that the substance functions as
molecular template by providing a template upon which, or
10   in relation to which, polymer subunits of the conductive
polymer preferentially align to induce orientation of the
subunits for forming the conductive polymer, and bonds to
or is entrapped within the non-conductive textile.

15   20.   The electroconductive textile of any one of claims 1
to 5, wherein:
       the macromolecular template is selected from the
group consisting of sulfonated polyanilines or derivatives
thereof, sulfonated polystyrenes or derivatives thereof,
20   dextran sulfate, calixarenes, cyclodextrins and
derivatives thereof, synthetic tanning agents based upon
sulfonated polycondensation products derived from aromatic
sulfonic acids or sulfones and formaldehyde, synthetic
tanning agents based upon polyacrylic-acid or salts or
25   esters thereof, polypropylene oxide polyurethane
shrinkproofing polymers containing reactive carbamoyl
sulfonate groups, sulfonated polypyrroles or derivatives
thereof, sulfonated polythiophenes or derivatives thereof,
and copolymers or mixtures of any of the above; and
30   the conductive polymer is selected from the group
consisting of polyaniline, polypyrrole, polythiophene,
polyphenyl mercaptan polyindole, polycarbazole or
derivatives or a copolymer or combination thereof.

35   21.   The electroconductive textile of any one of claims 1
to 20, wherein the non-conductive textile contains no
functionalisation which would enable a reaction forming a

covalent bond between the textile and the macromolecular template, and contains no phosphonylation.

22.   The electroconductive textile of any one of claims 1 to 21, wherein the non-conductive textile is formed from natural or synthetic fibers, or a combination thereof.

23.   The electroconductive textile of claim 22, wherein the non-conductive textile contains natural fibres.

24.   The electroconductive textile of any one of claims 1 to 23, wherein the electroconductive textile contains no curing binder.

25.   The electroconductive textile of any one of claims 1 to 24, comprising one or more further layers of conductive polymer.

26.   A method for preparing an electroconductive textile from a non-conductive textile and polymer subunits which, when polymerised, form a conductive polymer, the method comprising the steps of:
        (i) polymerising the polymer subunits in the presence of a macromolecular template to form the conductive polymer bound to the macromolecular template; and
        (ii) contacting the macromolecular template with the non-conductive textile to effect bonding of the macromolecular template to the non-conductive textile.

27.   The method of claim 26, wherein the macromolecular template is contacted with the non-conductive textile by padding, exhaustion, printing or coating techniques.

28.   The method of claim 26 or claim 27, wherein the macromolecular template is applied in an amount of between 0.1 and 50% on mass of fabric.

29.   The method of claim 28, wherein the macromolecular template is contacted with the non-conductive textile in an amount of 3-20% on mass of fabric.

5   30.   The method of claim 28, wherein the macromolecular template is applied to the non-conductive textile in an amount of between 5 and 10% on mass of fabric.

31.   The method of any one of claims 26 to 30, wherein,
10   prior to step (ii), the non-conductive textile is contacted with surfactant.

32.   The method of any one of claims 26 to 31, wherein step (ii) comprises contacting a solution of the
15   macromolecular template with the non-conductive textile at an initial solution pH of between 1.0-9.0.

33.   The method of claim 32, wherein the initial solution pH is between 1.0-2.7.
20

34.   The method of claim 32, wherein the initial solution pH is between 1.4 - 1.8.

35.   The method of any one of claims 26 to 34, wherein
25   step (ii) comprises contacting a solution of the macromolecular template with the non-conductive textile at a temperature of between 20 and 130°C.

36.   The method of claim 35, wherein step (ii) is
30   conducted by the exhaust technique.

37.   The method of claim 36, wherein the contact temperature is between 60 and 100°C, and the time of contact is a period of at least 30 minutes.
35

38.   The method of claim 36, wherein the contact temperature is between 80 and 100°C.

39.   The method of claim 37 or claim 38, wherein the time
of contact is at least 3 hours.

5   40.   The method of any one of claims 26 to 35, wherein
step (ii) is conducted by the padding technique.

41.   The method of claim 40, wherein step (ii) comprises
contacting a padding liquid containing 20-200 grams/litre
10   of the molecular template with the non-conductive textile.

42.   The method of claim 41, wherein the pH of the
padding liquid is between 1.0 - 1.8.

15   43.   The method of claim 41 or 42, wherein step (ii)
effects application of between 5 and 50% of the
macromolecular template on mass of the fabric.

44.   The method of any one of claims 26 to 43, wherein
20   the method comprises the steps of:
        (a) contacting the macromolecular template with the
non-conductive textile to effect bonding of the
macromolecular template to the non-conductive textile, and
        (b) contacting the polymer subunits with the
25   macromolecular template bound to the non-conductive
textile, and polymerising the polymer subunits to form the
conductive polymer bound to the macromolecular template
and to the non-conductive textile via the macromolecular
template.
30

45.   The method of claim 44, wherein the polymer subunits
are polymerised by adding an oxidizing agent.

46.   The method of claim 45, wherein the molar ratio of
35   the polymer sub units to the oxidant is between 1:0.16 and
1:0.5.

47.   The method of claims 44 to 46, wherein a solution of
the polymer subunits is contacted with the molecular
template bound to the non-conductive textile, and the pH
during contacting stage (b) is between 1.1 – 4.0.

48.   The method of claim 47, wherein the pH of contacting
step (b) is between 1.1 – 2.4.

49.   The method of claim 47, wherein the pH of the
contacting step (b) is between 1.1 – 1.8.

50.   The method of any one of claims 44 to 49, wherein
the polymer subunits are polymerized at ambient
temperature.

51.   The method of any one of claims 26 to 50, wherein
the molar ratio of macromolecular template to the polymer
subunits is between 1:1 and 1:40.

52.   The method of 51, wherein the molar ratio is about
1:2.

53.   The method of any one of claims 26 to 43, wherein
the method comprises the steps of:
        (a) contacting the non-conductive textile, the
macromolecular template and the polymer subunits with one
another to effect bonding of the macromolecular template
to the non-conductive textile, and bonding of the
macromolecular template to the polymer subunits, and
        (b) polymerising the polymer subunits to form the
conductive polymer which is bound to the non-conductive
textile via the macromolecular template.

54.   The method of claim 53, wherein step (a) involves
contacting a solution of the macromolecular template and
the polymer subunits with the non-conductive textile, and
step (b) comprises the addition of an oxidant to the

solution containing the non-conductive textile.

55.   The method of any one of claims 26 to 43, wherein
the method comprises the steps of:
       (a) contacting the macromolecular template with the
polymer subunits and polymerising the polymer subunits to
form the conductive polymer bound to the macromolecular
template, and
       (b) contacting the macromolecular template with the
non-conductive textile to effect bonding of the
macromolecular template to the non-conductive textile,
with the conductive polymer bound to the non-conductive
textile via the macromolecular template.

56.   The method of claim 55, wherein step (a) comprises
forming an aqueous solution of the macromolecular template
and the polymer subunits, reducing the pH of the solution
to a value between 1.1 - 2.4, and contacting the solution
with an oxidant.

57.   The method of claim 56, wherein the molar ratio of
polymer subunits to oxidant is between 2:1 and 1:1.

58.   The method of any one of claims 55 to 57, wherein
the molar ratio of macromolecular template to polymer
subunits is between 1:1 - 1:4.

59.   The method of any one of claims 26 to 58, wherein:
       the macromolecular template is selected from the
group consisting of sulfonated polyanilines or derivatives
thereof, sulfonated polystyrenes or derivatives thereof,
dextran sulfate, calixarenes, cyclodextrins and
derivatives thereof, synthetic tanning agents based upon
sulfonated polycondensation products derived from aromatic
sulfonic acids or sulfones and formaldehyde, synthetic
tanning agents based upon polyacrylic-acid or salts or
esters thereof, polypropylene oxide polyurethane

shrinkproofing polymers containing reactive carbamoyl
sulfonate groups, sulfonated polypyrroles or derivatives
thereof, sulfonated polythiophenes or derivatives thereof,
and copolymers or mixtures of any of the above; and

5   the conductive polymer is selected from the group
consisting of polyaniline, polypyrrole, polythiophene,
polyphenyl mercaptan polyindole, polycarbazole or
derivatives or a copolymer or combination thereof.

10   60.   An article formed partly or entirely from the
electroconductive textile of any one of claims 1 to 25.

61.   An article formed partly or entirely from the
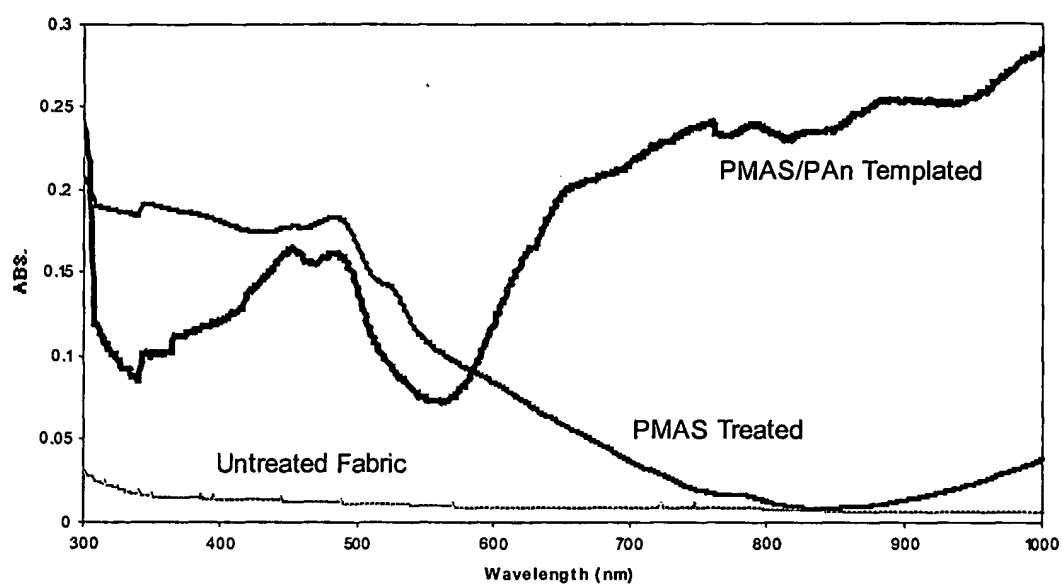electroconductive textile produced by the method of any
15   one of claims 26 to 59.

62.   The article of claim 60 or claim 61, wherein the
article is selected from gloves, car seats, heating panels
for car seats, protective clothing, hosiery, apparel
20   items, footwear, headgear, strange gauges, energy storage
devices and energy conversion devices.

Figure 1
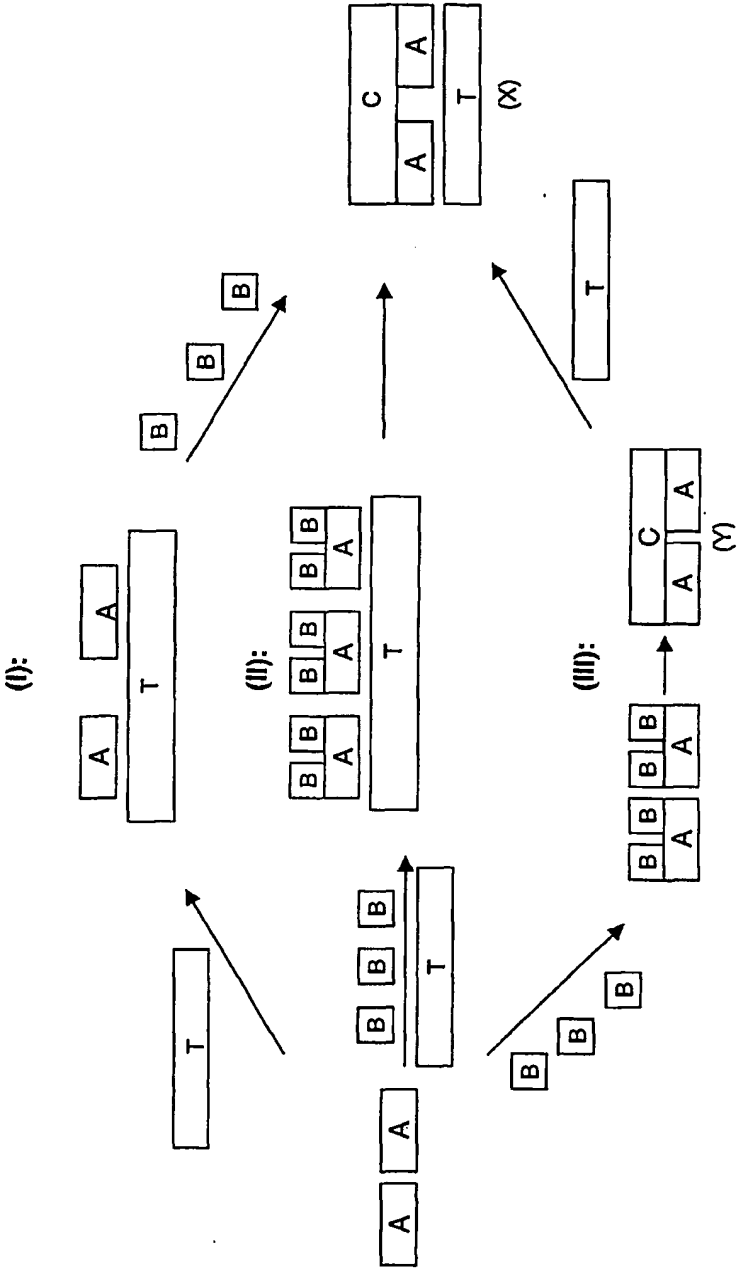
Figure 2:

INTERNATIONAL SEARCH REPORT

A.	CLASSIFICATION OF SUBJECT MATTER

Int. Cl. [7]: D06M 15/356

According to International Patent Classification (IPC) or to both national classification and IPC

B.	FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Derwent DWPI: IPC D06M and keywords CONDUCT, ELECTROCONDUCT, ELECTRO-CONDUCT

C.	DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Derwent Abstract Accession No. 93-121894/15, Class A32 F01 (A26 A85 F06), JP 05059671 A (ACHILLES CORP) 9 March 1993	
A	Derwent Abstract Accession No. 92-302539/37, Class X12, JP 04202856 A (ACHILLES CORP) 23 July 1992	
A	Derwent Abstract Accession No. 92-059251/08, Class U11, JP 03294580 A (ACHILLES CORP) 25 December 1991	
A	Derwent Abstract Accession No. 92-059250/08, Class U11, JP 03294579 A (ACHILLES CORP) 25 December 1991	

[X] Further documents are listed in the continuation of Box C	[X] See patent family annex

*	Special categories of cited documents:		
"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
27 August 2004	- 2 SEP 2004

Name and mailing address of the ISA/AU	Authorized officer
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C (Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Derwent Abstract Accession No. 89-353895/48, Class A85 F06 (A26 A87) JP 01266280 A (TORAY IND INC) 24 October 1989	
A	Derwent Abstract Accession No. 97-103987/10, Class A35 F06 G02 (A14 A26 A87) JP 08337972 A (ACHILLES CORP KK) 24 December 1924	
A	US 4975317 A (KUHN et al) 4 December 1990 See whole document	

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
JP	5059671	NIL					
JP	4202856	NIL					
JP	3294580	NIL					
JP	3294579	NIL					
JP	1266280	NIL					
JP	8337972	NIL					
US	4975317	EP	0302590	JP	2033381	US	4803096

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX